Quality Assurance Project Plan

Measuring Copper Concentrations in Two Puget Sound Marinas

by
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September 2006

303(d) Listings Addressed in this Study: None

Waterbody Number: WA-PS-0200 Rosario Strait
WA-PS-0020 Padilla Bay, Fidalgo Bay, Guemes Channel

Project Code: 07-115

Approvals

Approved by:	September 14, 2006
Gary Bailey, Client, WQP-HQ	Date
Approved by:	September 14, 2006
Nancy Winters, Section Manager, WQP-HQ	Date
Approved by:	September 12, 2006
Art Johnson, Project Lead, Toxics Studies Unit	Date
Approved by:	September 19, 2006
Carolyn Lee, EIM Data Engineer, Watershed Ecology Section	Date
Approved by:	September 12, 2006
Dale Norton, Unit Supervisor, Toxics Studies Unit	Date
Approved by:	September 12, 2006
Will Kendra, Section Manager, Watershed Ecology Section	Date
Approved by:	September 22, 2006
Stuart Magoon, Director, Manchester Environmental Laboratory	Date
Approved by:	September 13, 2006
Bill Kammin, Ecology Quality Assurance Officer	Date

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Abstract

A Quality Assurance Project Plan is provided for measuring dissolved copper concentrations at two Puget Sound marinas. Sampling will be conducted during periods of minimal tidal exchange in the summer and winter of 2006/2007. Low-level methods will be used to characterize dissolved copper concentrations inside and outside the marinas and to determine if Washington State criteria for protection of marine life are exceeded.

Background

Marinas are potentially large sources of metals—especially copper—to marine waters. Young et al. (1979) was among the first to identify vessels and harbor-related activities as significant sources of copper to nearshore ecosystems. The copper comes primarily from antifouling paints which are designed to discourage barnacles, mussels, and other organisms from attaching to boat hulls. Copper is also released through underwater hull cleaning, a frequent practice. Copper is the most common pollutant found at toxic levels in marinas nationwide (USEPA, 1993).

Recently, the Shelter Island Yacht Basin (SIYB) in San Diego Bay was designated as an impaired waterbody for dissolved copper, pursuant to Clean Water Act Section 303(d). SIYB is a semi-enclosed yacht basin comprised of recreational marinas and yacht clubs. The California Regional Water Quality Control Board recently conducted a Total Maximum Daily Load (TMDL) study for copper in SIYB (CRWQCB, 2005). Field surveys showed dissolved copper concentrations averaging 8.0 μg/L (parts per billion) and reaching as high as 12 μg/L. The copper levels in SIYB exceeded California and EPA water quality criteria and have been associated with adverse effects on the biota. A TMDL was adopted to address this impairment.

Copper has been analyzed in several historical studies of Puget Sound marinas. Cardwell et al. (1980a,b) found higher copper concentrations in oysters and sediment inside five Puget Sound marinas than outside. The same studies documented poor flushing of marinas. Skyline Marina on Fidalgo Island was singled out as an example, with only 8-40% of the water being exchanged over a 12-hour period.

Crecelius et al. (1989) measured contaminant loadings to Puget Sound from two marinas: the Port of Port Townsend Marina and Cap Sante Marina in Anacortes. They concluded that the water and sediment inside the marinas "were contaminated with copper…compared to samples taken outside the marinas." Copper concentrations in water samples collected at the marina entrances were significantly higher at ebb than flood, ranging from 1.3 – 5.6 μg/L (total recoverable). Washington's current chronic and acute criteria for copper are 3.1 and 4.8 μg/L (as dissolved), respectively (WAC 173-201A). Crecelius et al. observed that most of the sediments in these marinas exceeded Puget Sound Dredge Disposal Analysis screening levels in effect at that time.

Project Description

The Washington State Department of Ecology (Ecology) Water Quality Program (WQP) wants to determine what dissolved copper concentrations currently exist in waters inside Puget Sound marinas. In response to this request, the Ecology Environmental Assessment (EA) Program will analyze water samples from two large Puget Sound marinas during the summer and winter of 2006/2007. Sampling will be conducted during periods of minimal tidal exchange. Forty-eight samples are planned.

The goal of the project is to provide the WQP with data that can be used to determine if copper levels in and around marinas represent a significant toxicity concern. Specific objectives of the study will be to:

1. Characterize dissolved copper concentrations in water inside the marinas.
2. Compare dissolved copper concentrations inside and outside the marinas.
3. Assess seasonal variation in dissolved copper concentrations.
4. Determine if Washington State water quality criteria are exceeded.

Organization and Schedule

Organization

Name	Organization	Phone No.	Role
Art Johnson	EAP-WES-TSU	360-407-6766	Project lead
Gary Bailey	WQP-HQ	360-407-6433	Client
Kristin Kinney	EAP-WES-TSU	360-407-7168	Field assistance
Dale Norton	EAP-WES-TSU	360-407-6765	Unit supervisor
Dean Momohara	Manchester Laboratory	360-871-8808	Unit supervisor
Stuart Magoon	Manchester Laboratory	360-871-8801	Lab director
Bill Kammin	EAP	360-407-6964	QA officer
Carolyn Lee	EAP-WES-TSU	360-407-6430	EIM data entry

Schedule

Sampling and Laboratory Analysis	
Field Work	August 2006; March 2007
Laboratory Analyses Completed	September 2006; April 2007
Final Report	
Report Author Lead	Art Johnson
Schedule:	
Report Supervisor Draft Due	May 2007
Report Client/Peer Draft Due	June 2007
Report External Draft Due	N/A
Report Final Due (Original)	July 2007
Environmental Information System (EIM) Data Set	
EIM Data Engineer	Carolyn Lee
EIM User Study ID	AJOH0051
EIM Study Name	Marina Copper Study
M Completion Due	July 2007

Quality Objectives

Quality objectives for this project are to obtain data of sufficient quality so that uncertainties are minimized and results are comparable to Washington State water quality criteria. These objectives will be achieved through careful attention to the sampling, measurement, and quality control (QC) procedures described in this plan.

Measurement Quality Objectives

Manchester Environmental Laboratory (MEL) and their contractors are expected to meet all QC requirements of the analytical methods being used for this project. Measurement quality objectives (MQOs) are shown in Table 1. These correspond to MEL's QC limits for percent recovery and precision. The lowest concentrations of interest for copper are set at one tenth the chronic water quality criterion, as recommended by Lombard and Kirchmer (2004).

Table 1. Measurement Quality Objectives for Marina Copper Study

Analysis	Check Stds./ Lab Control Samples (% recov.)	Duplicate Samples (RPD)	Matrix Spikes (% recov.)	Matrix Spike Duplicates (RPD)	Lowest Concentration of Interest
Dissolved Copper	85-115%	20%	75-125%	20%	0.3 ug/L
TSS	80-120%	20%	NA	NA	1 mg/L
Salinity	80-120%	20%	NA	NA	0.1 g/Kg

RPD = relative percent difference
NA = not applicable

Sampling Design

Marina configuration and size are expected to be the major factors influencing copper concentrations. The selection criteria for marinas to be sampled generally follow the Crecelius et al. (1989) study:

1. A single entrance channel to an enclosed marina
2. Greater than 500 boats
3. No major marina construction in the last three years
4. No other significant metals sources in the immediate vicinity

Based on these criteria and logistical considerations imposed by the need to sample the same tide stage at two sites, Cap Sante Boat Haven (1,050 slips) and Skyline Marina (>500, exact number not known at this time) were selected for sampling. Both of these marinas are in or near Anacortes (Figures 1-3). Both have been the subject of historical water quality studies that included copper, as previously described.

Cap Sante Boat Haven
Port of Anacortes
P.O. Box 297
Anacortes, WA 98221
(marina@portofanacortes.com)
360-293-0694
Dale Fowler, Harbormaster

Skyline Marina
2011 Skyline Way 203
Anacortes, WA 98221 - 2986
306-293-5134
Kelly Larkin, Manager

It is assumed that the highest copper concentrations occur in the summer when boating activity is at its peak. Most boaters apply bottom paint in the spring to early summer; June is the busiest month at most boat yards. Concentrations would be expected to decrease over time as paints leach and hulls get foul.

Water samples will be collected during a neap tide series in August 2006 and again in March 2007. The August samples are intended to approximate worst-case conditions. The March samples may allow conclusions to be drawn about seasonal changes in copper concentrations.

The samples will be collected at the marina entrance during the last half of the ebb and last half of the flood. Sampling the entrance at ebb should give more representative data than collecting at some point inside the marina. The flood samples are intended to reflect local background and will be simpler to collect and more directly applicable to assessing marina impacts than if taken by going offshore.

The sampling design for the study is summarized in Table 2. Six ebb and six flood samples will be collected at each marina over a three-day period during August 2006 and again during March 2007. A total of 54 samples, including QC samples, is planned for the study.

Table 2. Sampling Design for Marina Copper Study
[number of samples to be collected during August 2006 and again during March 2007]

Sample Day	Day-1	Day-1	Day-2	Day-2	Day-3	Day-3	
Tide Stage	Ebb	Flood	Ebb	Flood	Ebb	Flood	Subtotals
Marina #1	2	2	2	2	2	2	12
Marina #2	2	2	2	2	2	2	12
Subtotals	4	4	4	4	4	4	24
Splits	1	1					2
Transfer Blank	1						1
Subtotals	6	5	4	4	4	4	27

Total Samples for Study (x2) = 54

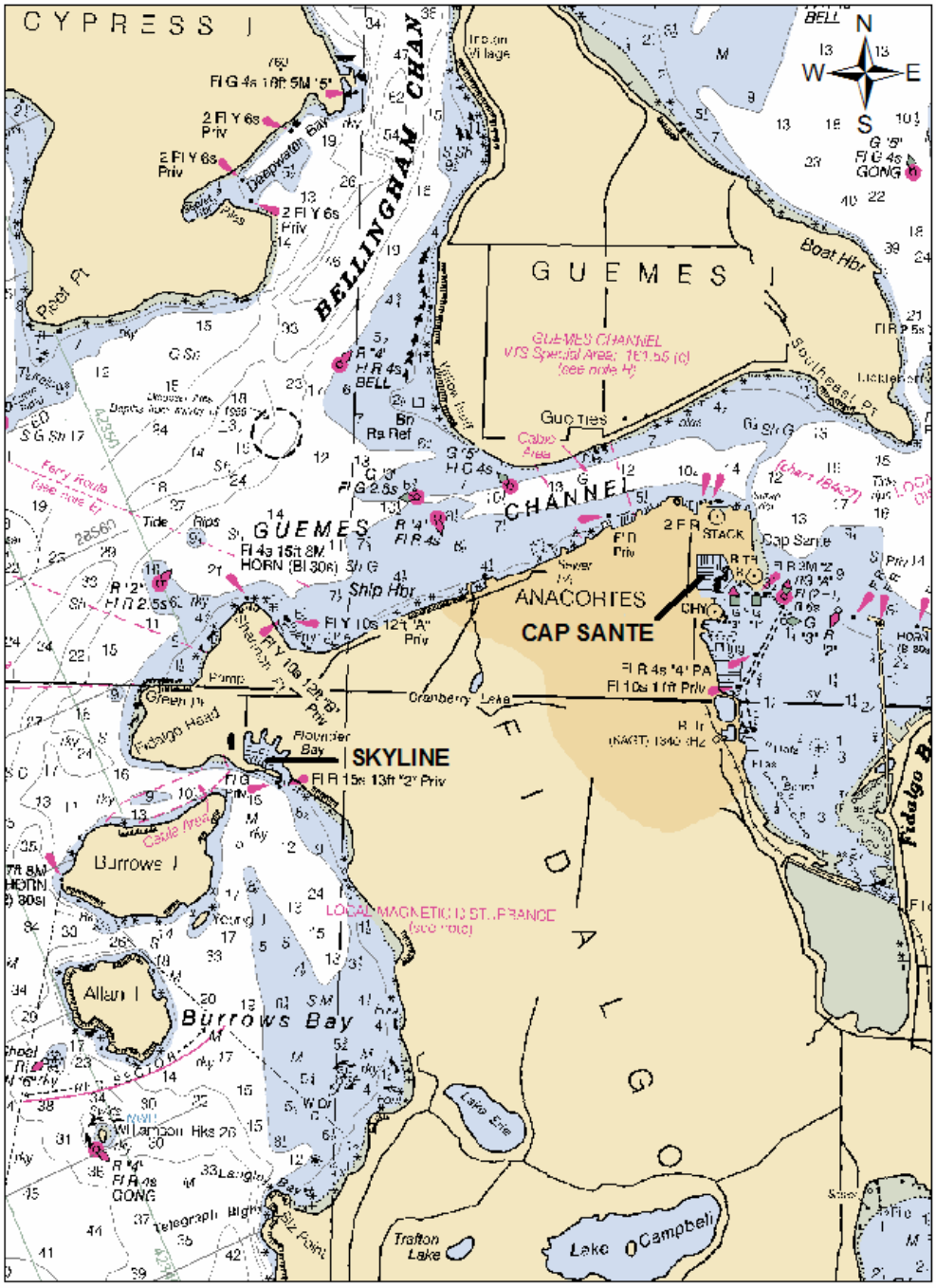

Figure 1. Anacortes Area, Showing Location of Cap Sante and Skyline Marinas

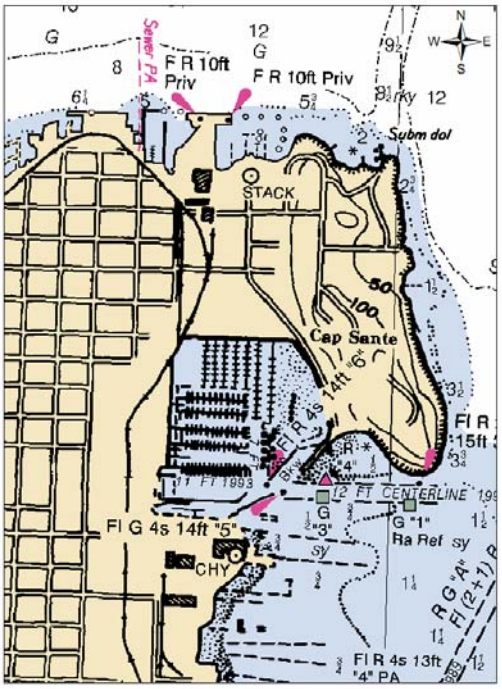

Figure 2. Cape Sante Marina, Anacortes

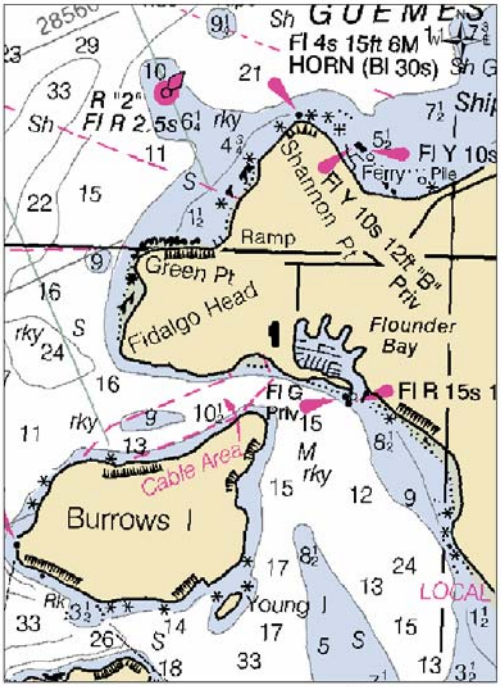

Figure 3. Skyline Marina, Anacortes

Sampling Procedures

Table 3 lists the sample size, container, preservation, and holding time for each parameter. Sample containers will be obtained from the analyzing laboratory.

Table 3. Field Procedures for Marina Copper Study

Parameter	Min. Sample Size	Container	Preservation	Holding Time
Copper	500 mL	500 mL Teflon bottle	Cool to 4°C*	6 months**
TSS	1000 mL	1 L poly bottle	Cool to 4°C	7 days
Salinty	300 mL	500 mL poly bottle	HCl to pH<2, 4°C	28 days

*to be filtered and acidified at the laboratory within 24 hours of collection
**acidified sample

Sampling methods for copper will follow the guidance in EPA Method 1669: *Sampling Ambient Water for Trace Metals at EPA Water Quality Criteria Levels*. Field personnel will wear non-talc nitrile gloves and take care not to introduce contamination in the samples. The copper, TSS, and salinity samples will be taken from a small boat (unpainted hull) in the center of the entrance channel. The samples will be collected from the bow by hand, directly into the sample bottles, with the boat facing the current.

The samples will be quickly sealed and labeled, put in double polyethylene bags, and placed in a cooler with ice. The copper samples will be transported directly to the analyzing laboratory within 24 hours of collection. The TSS and salinity samples will be held on ice for next day transport to MEL. Chain of custody will be maintained.

Water temperature at the time of sample collection will be taken with a precision thermometer. The latitude and longitude of each sampling site will be recorded from a GPS.

Measurement Procedures

Due to the high salt content, special analytical methods are required to measure copper in seawater. MEL has selected Frontier Geosciences to analyze the samples using coprecipitation with Co-APDC and analysis by ICP-MS (EPA Method 1638). This technique removes the metals of interest from the high-salt matrix and provides a 20-fold concentration of the sample. Detection limits of 0.02 μg/L are reported to be achievable for copper by this method (www.fgsdata.com). The dissolved copper background in the Anacortes area is around 0.4 μg/L (Crecelius, 1998). The copper samples will be filtered and acidified at Frontier within 24 hours of collection (EPA Method 1640).

The TSS and salinity samples will be analyzed at MEL following Standard Methods 2540D and 2520, respectively.

The laboratory costs for this project are estimated to be $10,500.

Quality Control Procedures

Table 4 shows the numbers and types of QC samples to be analyzed for this project.

Table 4. QC Samples for Marina Metals Study

	Field		Laboratory				
Parameter	Transfer Blanks	Duplicate Samples	Filter Blanks	Check Std./ LCS	Method Blanks	MS/ MSD	SRM
Copper	2/project	4/project	2/project	1/batch	1/batch	1/batch	1/batch
TSS	NA	4/project	NA	1/batch	1/batch	NA	NA
Salinity	NA	4/project	NA	1/batch	1/batch	NA	NA

Field

Field QC for this project will include transfer blanks for copper and duplicate (split) samples for copper, TSS, and salinity.

The transfer blanks are intended to detect contamination arising from sample containers or sample handling. The blanks will be prepared using a sample bottle filled with blank water by Frontier Geosciences. The bottle will be opened in the field and its contents transferred to a new bottle, in essence mimicking the grab sampling procedure.

Duplicates will provide estimates of analytical variability. The duplicates will be prepared by filling two sample bottles from the same grab.

The transfer blanks and duplicate samples will be submitted blind to the laboratory.

Laboratory

Laboratory QC samples for copper will include filter blanks, check standards/laboratory control samples, method blanks, matrix spikes and matrix spike duplicates, and a standard reference material (SRM). The SRM will be CASS-4 Nearshore Seawater Reference Material for Trace Metals (National Research Council Canada) or an equivalent SRM. The CASS-4 certified value for copper is 0.592 ± 0.055 ug/L.

Laboratory QC samples for TSS and salinity will follow routine MEL practice.

Data Management Procedures

Field data will be recorded in a bound notebook of waterproof paper.

The data packages from MEL will include a case narrative discussing any problems with the analyses, corrective actions taken, changes to the referenced method, and an explanation of data qualifiers. The data package should also include all associated QC results. This information is needed to evaluate the accuracy of the data and to determine whether the MQOs were met. This should include results for all blanks, check standards/LCS samples, matrix spikes, duplicates, and SRMs included in the sample batch.

All project data will be entered into Excel spreadsheets. All entries will be independently verified for accuracy by another individual on the unit.

All project data will be entered into Ecology's Environmental Information Management System (EIM). Data entered into EIM follow a formal Data Validation Review Procedure where data is reviewed by the project manager of the study, the person entering the data, and an independent reviewer.

Audits and Reports

Audits

MEL participates in performance and system audits of their routine procedures. Results of these audits are available on request.

Reports

A draft project report will be prepared for the client and other interested parties. The tentative data for this report is June 2007. A final technical report is anticipated on or before July 2007. The responsible staff member is Art Johnson.

The project data will be entered into EIM on or before July 2007. The responsible staff member is Carolyn Lee.

Data Verification and Validation

MEL will conduct a review of all laboratory data and case narratives. MEL will verify that methods and protocols specified in this Quality Assurance Project Plan were followed; that all calibrations, checks on quality control, and intermediate calculations were performed for all samples; and that the data are consistent, correct, and complete, with no errors or omissions. Evaluation criteria will include the acceptability of holding times, instrument calibration, procedural blanks, spike sample analyses, precision data, laboratory control sample and SRM analyses, and appropriateness of data qualifiers assigned. MEL will prepare written data verification reports based on the results of their data review. A case summary can meet the requirements for a data verification report.

To determine if project MQOs have been met, results for check standards/LCS, duplicate samples, matrix spikes, and the SRM will be compared to QC limits. The method blanks' results will be examined to verify there was no significant contamination of the samples. To evaluate whether the targets for reporting limits have been met, the results will be examined for non-detects and to determine if any values exceed the lowest concentration of interest.

The project lead will review the laboratory data packages and MEL's data verification report and validate the data. Based on these assessments, the data will be either accepted, accepted with appropriate qualifications, or rejected and re-analysis considered.

Data Quality (Usability) Assessment

Once the data have been verified and validated, the project lead will determine if they can be used to make the calculations, determinations, and decisions for which the project was conducted. If the results are satisfactory, data analysis will proceed.

Descriptive statistics and box plots will be examined to evaluate the distribution of copper concentrations in the study area. Parametric or non-parametric statistical tests, as appropriate, will be used to compare mean concentrations between marinas, ebb and flood, and seasons. The copper concentration/water quality criteria ratio will be calculated for each sample and displayed in dot density plots to illustrate the extent to which criteria are, or are not, exceeded.

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